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Cover Page Footnote
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EXPERIMENTAL AND BIOGEOCHEMICAL MODELING STUDIES ON ARSENIC RELEASE IN SOIL UNDER ANAEROBIC CONDITION

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ABSTRACT

The identification of release mechanism of arsenic may assist in designing safe and effective remediation strategies, due to its severe toxicity effect for the human body. In this regards, investigations were carried out to observe the release of As from soil into water. It was found that As concentration increased with decreasing oxidation reduction potential. Arsenic concentrations demonstrated negative covariation with the concentrations of NO_3^- but strongly correlated with DOC and Fe concentrations. Batch leaching tests at different pH conditions showed a strong pH dependence on arsenic and iron leaching. A numerical simulation of arsenic transport model, coupled with microbially mediated biogeochemical processes was developed for describing the release of As in soil under reducing environment. The simulation concentrations of Mn, Fe and As were well matched those found experimentally. The results of this study suggested that the microbially mediated degradation of organic matter and reductive dissolution of Fe-oxyhydroxide are considered to be the dominant processes to release As in aquifers.

2. INTRODUCTION

Groundwater is the major source of water supply for domestic consumption, agriculture and industrial development, due to its inherent features. Unfortunately, groundwater is affected by arsenic (As) and now it is major concern on a global scale due to its severe toxicity effect for the human body. The chemical species arsenate [As(V)] and arsenite [As(III)] of As controlling its chemistry and toxicity in the environment. Arsenate is the thermodynamically stable form under aerobic conditions and it is mainly adsorbed onto iron and manganese oxides. Arsenite is the predominate species under anaerobic conditions; it is a neutral species at neutral pH values and is more soluble, mobile and phytotoxic than arsenate (Carbonell-Barrachina et al., 1999).

The mobilization of arsenic from soil to groundwater and groundwater to soil is dependent on soil-water interaction in the subsoil environment. Although the geogenic source of As in the groundwater is generally accepted, the primary source and mechanism of release of As from soils and aquifer sediments into the groundwater is still not well understood (Wagner et al.

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2005). However, the reductive dissolution of arsenic-rich iron and manganese oxyhydroxides deeper in the aquifer may lead to the release of arsenic into the ground water is highly acceptable (Smedley and Kinniburgh, 2002). On-site hydro-chemical investigations of aquifers have led to the hypothesis that the mobility of arsenic is primarily controlled by the availability of organic matter, which drives this process forward through microbial degradation of organic matter after consumed dissolved-O_2 and NO_3^- (Nickson et al., 2000), although this hypothesis has not been rigorously proven. It is not clear if theses organic matters are derived from decomposing buried peat beds or from hydrologic seasonal drawdown of agricultural and other organic waste from the surface (McArthur et al. 2004).

The oxidation reduction potential (ORP) can affect the degradation and solubility of such organic material those are living in soil and then influence the release of As in groundwater. Arsenic is chemically and microbiologically mediated oxidation-reduction, and methylation reaction in soils (Masscheleyn et al., 1991). It is necessary to develop a comprehensive reactive transport model that can simultaneously describe microbially-mediated biogeochemical reactions as well as other advection-dispersion processes. However, some studies on arsenic reactive transport have considered either adsorptive transport under anaerobic conditions or equilibrium sorption (Darland and Inskeep, 1997; Williams et al., 2003). None of these studies have considered the effects of microbial reaction kinetics.

The main objectives of this study are: (i) to conduct the experiments for elucidating the effect of oxidation reduction potential, pH and dissolved organic matter on release of arsenic from soil into groundwater, and (ii) to develop a biogeochemical arsenic transport model that consider microbially mediated redox processes for evaluating experimental results.

3. MATERIALS AND METHODS

3.1 Laboratory experiments

A column experiment was carried out to observe the release of arsenic from soil to water under anaerobic environment. Air-dried sediment sample was added with original soil at around 5% of total samples to enhance organic matter, manganese, iron and arsenic. The major physicochemical properties of the study soil together with original soil are given in Table 1. The pH of these samples was measured in 1:2 soil to deionized water ratio.

Table 1. Main physicochemical properties of the study soil together with original soil.

Parameter	Original soil	Study soil
TOC (%)	1.70	1.95
pH	6.2	6.2
ORP (mV)	345	359
Fe (mg/kg)	17000	39400
Mn (mg/kg)	2.3	1130
As(III) (mg/kg)	BDL	BDL
As(V) (mg/kg)	6.4	9.4
As_{total} (mg/kg)	6.4	9.4

TOC: Total Organic Carbon, ORP: Oxidation Reduction Potential

BDL: Bellow Detection Limit (0.5 mg/l)

A schematic diagram of experimental setup is shown in Fig. 1. The apparatus consisted transparentacryl Resin column of 10 cm in diameter and 30 cm in height. The column was packed with study soil of 3.5 kg and its surface area, bed volume and total bed porosity were 78.54 cm^2, 2356 cm^3 and 44%, respectively. The top and the bottom of the column were closed using glass transparentacryl Resin plates with tubes for the flowing of influent and effluent, respectively. The water flow was continuous from feeding tank point 1 to overflow tank point 3 to create the anaerobic environment in the soil column and average temperature was measured at 24 ^{0}C.

At point 5, effluents were collected in the clean air tied disposable syringe coupled with filtration unit of 0.45 μm pore size. All effluents were kept in the refrigerator at 4 ^{0}C for analyzing. The pH and oxidation reduction potential (ORP) of the examined water were 7.9 and 301 mV, respectively. The amounts of total As, Fe and Mn in this water were 1.2, 1.6 and 2.3 μg/l respectively.

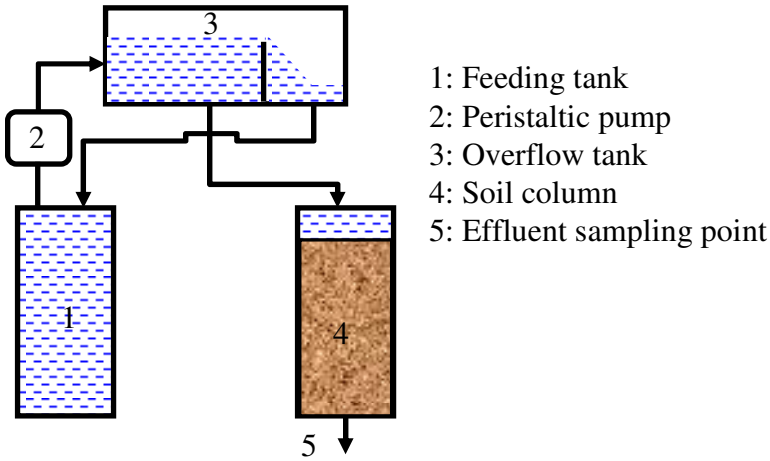

Figure 1. Schematic diagram of the experimental setup for the column tests.

Batch experiments at different pH values of 1 to 13 were carried out to observe the As release from soil to groundwater. Supra-pure grads HNO_3 and ultra-pure grade NaOH were used for adjusting the pH of solutions. All experiments were conducted by combining 30 ml of pH solution with 0.5 g of soil in 60 ml polypropylene bottle at a liquid:solid ratio of 60:1. The samples were then shaken for 48 hours at room temperature. The suspensions were subsequently sampled and flitted through 0.45 μm pore size filtration unit and the supernatants were analyzed for iron and arsenic.

3.2 Analytical determinations

The measurements of oxidation reduction potential (ORP), conductivity (EC), temperature and pH were performed immediately after effluent collection. The Redox Meter (TOA, RM-20P) using two electrodes (Ag/AgCl and platinum) was employed for the measurement of ORP. Dissolved organic carbon (DOC) was measured by high-temperature catalytic oxidation method using a Shimazu TOC 5000A, total organic carbon analyzer. The total concentrations of As, Fe and Mn in the samples were measured by inductively coupled plasma and mass spectrometry (ICP-MS) (Agilent 7500, Octopole reaction system). The mass resolution was low that produced

high-peak intensities. The instrument was linearly calibrated from 10 to 100 μg l^{-1} with custom multi-element standard (SPEX CertiPrep, Inc.). The detection limit of the instrument for As was 6 ng/l. The average relative standard deviation for all the samples was 5%. All of the samples were diluted several times to adjust for the operating range and were analyzed.

3.3 Biogeochemical modeling

3.3.1 Conceptual model

The model developed in this study was based on the reactive solute transport and biogeochemical reaction processes. This model takes into account three different phases: mobile pore water phase, immobile bio phase and matrix phase, which shown in Fig. 2 with chemical species considered in the model. All biogeochemical reactions take place inside the bio phase. Five different species of bacteria *X1*, *X2*, *X3*, *X4* and *X5* are assumed to grow in this bio phase.

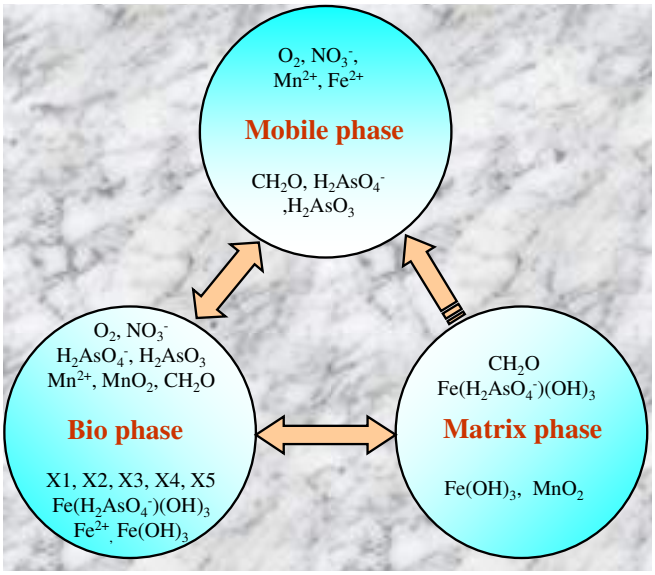

Figure 2. Conceptual biogeochemical model of arsenic mobilization in soil.

Table 2. Microbials and biochemical reactions used for simulation of As reduction in soil.

Bacteria		Reaction
X1	Aerobic	$CH_2O + O_2 \rightarrow CO_2 + H_2O$
	Denitrifying	$5CH_2O + 4\ NO_3^- + 4H^+ \rightarrow 5CO_2 + 2N_2 + 2H_2O$
X2	Manganese reducing	$CH_2O + 2MnO_2 + 3H^+ \rightarrow HCO_3^- + 2Mn^{2+} + 2H_2O$
X3	Iron reducing	$CH_2O + 4Fe(OH)_3 + 7H^+ \rightarrow HCO_3^- + 4Fe^{2+} + 10H_2O$
X4	Dissolution of surface complexation	$CH_2O + 4Fe(OH)_3(H_2AsO_4^-) + 2H_2O \rightarrow HCO_3^- + 4Fe^{2+} + 2H_2AsO_4^- + 6H^+$
X5	Arsenic reducing	$CH_2O + H_2AsO_4^- + H^+ \rightarrow HCO_3^- + 2H_3AsO_3$

In the conceptual model, the arsenic transformation reaction is modeled as an oxidation-reduction process, where a carbonaceous substrate is oxidized to supply the required electrons and As(V) is reduced by acting as an electron accepter. The As(V) reduction process is incorporated within a sequential terminal electron acceptor reaction modeling framework,

including aerobic, denitrifying, Mn(IV)-reducing, Fe(III)-reducing, dissolution of surface complexation and As(V)-reducing processes. Using organic matter as the ultimate electron donor and O_2, NO_3^-, Mn(IV), Fe(III) and As(V) as electron acceptors, the different degradation biochemical reaction processes are shown in Table 2.

3.3.2 Mathematical model

The transport part of the model solves the one dimensional advection dispersion partial differential equation for each chemical species. Following mass transport equation is used for the numerical modeling of the pollutants transport (Bear, 1972):

$$\frac{dC_i}{dt} = \frac{\partial C_i}{\partial t} + \frac{\partial}{\partial x_m}\left(C_i V_m\right) = \frac{\partial}{\partial x_m}\left(D_{L_{mn}} \frac{\partial C_i}{\partial x_n}\right) + f(C_j) \tag{1}$$

where, C_i = target concentration of dissolved species i(ML^{-3}), D_{Lmn} = coefficient of hydraulic dispersion (L^2T^{-1}), $Vm = q_m / n_e$ = pore velocity of the ground water in the direction of x_m(LT^{-1}), C_j = concentration of interacting species through source/sink term $f(C_j)$ representing bio-chemical reactions term.

Exchange processes are considered between the different model phases. The exchange between two phases is modeled by a linear exchange term. Mass exchange of dissolved species is governed by the concentration difference of the species in the pore water phase $[C_j]_{mob}$, the bio phase $[C_j]_{bio}$, the matrix phase $[C_j]_{mat}$, and the exchange coefficients α, β, and γ formulated as (Schäfer et al., 1998; Lensing et al., 1994):

$$C_1 = \frac{\alpha\theta_{bio}}{\theta_{bio} + \theta_w}\left(\left[C_i\right]_{bio} - \left[C_i\right]_{mob}\right) \tag{2}$$

$$C_2 = \frac{\beta\theta_{mat}}{\theta_{mat} + \theta_w}\left(\left[C_i\right]_{mat} - \left[C_i\right]_{mob}\right) \tag{3}$$

$$C_3 = \frac{\gamma\theta_{mat}}{\theta_{mat} + \theta_w}\left(\left[C_i\right]_{bio} - \left[C_i\right]_{mat}\right) \tag{4}$$

where, C_1 is the term of exchange reaction at the concentration difference between the pore and the bio phase, C_2 is the exchange reaction term at the concentration difference between pore water and soil matrix, and C_3 is the exchange reaction term between matrix phase and the bio phase. θ_w, θ_{bio} and θ_{mat} are the specific volume of mobile phase, bio phase and matrix phase, respectively.

For the chemical species related to As(III) and As(V) the following equations are formulated:

Mobile phase: $H_2AsO_4^-$:

$$\frac{\partial[H_2AsO_4^-]_{mob}}{\partial t} + v\frac{-\partial[H_2AsO_4^-]_{mob}}{\partial x} = D_L \frac{\partial^2[H_2AsO_4^-]_{mob}}{\partial x^2} + \frac{\alpha\theta_{bio}}{\theta_{bio} + \theta_w}\left([H_2AsO_4^-]_{bio} - [H_2AsO_4^-]_{mob}\right) \tag{5}$$

H_3AsO_3:

$$\frac{\partial[H_3AsO_3]_{mob}}{\partial t} + \bar{v}\frac{\partial[H_3AsO_3]_{mob}}{\partial x} = D_L\frac{\partial^2[H_3AsO_3]_{mob}}{\partial x^2} + \frac{\alpha\theta_{bio}}{\theta_{bio}+\theta_w}\left([H_3AsO_3]_{bio} - [H_3AsO_3]_{mob}\right) \quad (6)$$

Bio phase: $H_2AsO_4^-$:

$$\frac{\partial[H_2AsO_4^-]_{bio}}{\partial t} = \frac{1}{P_{H_2AsO_4^-}}\left[\frac{\partial X_4}{\partial t}\right]_{growth} - \frac{1}{U_{H_2AsO_4^-}}\left[\frac{\partial X_5}{\partial t}\right]_{growth} - \frac{\alpha\theta_w}{\theta_{bio}+\theta_w}\left([H_2AsO_4^-]_{bio} - [H_2AsO_4^-]_{mob}\right) \quad (7)$$

H_3AsO_3:

$$\frac{\partial[H_3AsO_3]_{bio}}{\partial t} = \frac{1}{P_{H_3AsO_3}}\left[\frac{\partial X_5}{\partial t}\right]_{growth} - \frac{\alpha\theta_w}{\theta_{bio}+\theta_w}\left([H_3AsO_3]_{bio} - [H_3AsO_3]_{mob}\right) \quad (8)$$

Fe $(H_2AsO_4^-)(OH)_3$:

$$\frac{\partial[Fe(H_2AsO_4^-)(OH)_3]_{bio}}{\partial t} = -\frac{1}{U_{Fe(H_2AsO_4^-)(OH)_3}}\left[\frac{\partial X_5}{\partial t}\right]_{growth} - \frac{\gamma\theta_{mat}}{\theta_{bio}+\theta_{mat}}\left([Fe(H_2AsO_4^-)(OH)_3]_{bio} - [Fe(H_2AsO_4^-)(OH)_3]_{mat}\right) \quad (9)$$

Matrix phase: $Fe(H_2AsO_4^-)(OH)_3$:

$$\frac{\partial[Fe(H_2AsO_4^-)(OH)_3]_{mat}}{\partial t} = \frac{\gamma\theta_{bio}}{\theta_{bio}+\theta_{mat}}\left([Fe(H_2AsO_4^-)(OH)_3]_{bio} - [Fe(H_2AsO_4^-)(OH)_3]_{mat}\right) \quad (10)$$

Bacteria: Bacteria X_4:

$$\left[\frac{\partial X_4}{\partial t}\right]_{Total\_growth} = \left[\frac{\partial X_4}{\partial t}\right]_{growth} + \left[\frac{\partial X_4}{\partial t}\right]_{decay} \quad (11)$$

$$\left[\frac{\partial X_4}{\partial t}\right]_{growth} = \nu_{\max}^{Fe(H_2AsO_4^-)(OH)_3}\cdot\frac{IC_{(O_2,NO_3^-)}}{IC_{(O_2,NO_3^-)}+[O_2,NO_3^-]_{bio}}\cdot\frac{IC_{Fe(OH)_3}}{IC_{Fe(OH)_3}+[Fe(OH)_3]_{bio}} \times\frac{[CH_2O]_{bio}}{K_{CH_2O}+[CH_2O]_{bio}}\cdot\frac{[Fe(H_2AsO_4^-)(OH)_3]_{bio}}{K_{H_2AsO_4^-}+[Fe(H_2AsO_4^-)(OH)_3]_{bio}}\cdot X_4 \quad (12)$$

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$$\left[\frac{\partial X_4}{\partial t}\right]_{decay} = -\nu_{X_4 dec} \cdot X_4 \tag{13}$$

Table 3. Parameters used for the simulation of arsenic reduction in the soil column.

Biochemical parameter		Value
Exchange coefficient	α	10.0 day^{-1}
	β	0.005 day^{-1}
	γ	0.00005 day^{-1}
Half velocity concentration	Half velocity of CH_2O	0.01 mmol/l
	Half velocity of O_2, NO_3^- and FeAs	0.001 mmol/l
	Half velocity of Mn, Fe and As	0.0001 mmol/l
Aerobic bacteria (*X1*)	Yield coefficient for organic carbon	0.3 mol cell-C/mol OC
	Maximum growth rate	3.0 day^{-1}
	Constant decay rate	0.3 day^{-1}
Denitrifying bacteria (*X1*)	Yield coefficient for organic carbon	0.027 mol cell-C/mol OC
	Maximum growth rate	1.125 day^{-1}
	Constant decay rate	0.1125 day^{-1}
Manganese reducing bacteria (*X2*)	Yield coefficient for organic carbon	0.21 mol cell-C/mol OC
	Maximum growth rate	0.26 day^{-1}
	Constant decay rate	0.026 day^{-1}
Iron reducing bacteria (*X3*)	Yield coefficient for organic carbon	0.16 mol cell-C/mol OC
	Maximum growth rate	0.75 day^{-1}
	Constant decay rate	0.025 day^{-1}
Dissolutive bacteria (X4)	Yield coefficient for organic carbon	0.01 mol cell-C/mol OC
	Maximum growth rate	0.89 day^{-1}
	Constant decay rate	0.089 day^{-1}
Arsenic reducing bacteria (*X5*)	Yield coefficient for organic carbon	0.01 mol cell-C/mol OC
	Maximum growth rate	0.1 day^{-1}
	Constant decay rate	0.01 day^{-1}
Switching function parameter	Threshold concentration of O_2	0.015 mmol/l
	Slope of switch function	40.0
Soil properties	Porosity	44.0%
	Longitudinal dispersion length	0.001 cm

Bacteria X_5:

$$\left[\frac{\partial X_5}{\partial t}\right]_{Total\_growth} = \left[\frac{\partial X_5}{\partial t}\right]_{growth} + \left[\frac{\partial X_5}{\partial t}\right]_{decay} \tag{14}$$

$$\left[\frac{\partial X_5}{\partial t}\right]_{growth} = \nu_{\max}^{H_2AsO_4^-} \cdot \frac{IC_{(O_2,NO_3^-)}}{IC_{(O_2,NO_3^-)} + [O_2, NO_3^-]_{bio}} \times \frac{[CH_2O]_{bio}}{K_{CH_2O} + [CH_2O]_{bio}} \cdot \frac{[H_2AsO_4^-]_{bio}}{K_{H_2AsO_4^-} + [H_2AsO_4^-]_{bio}} \cdot X_5 \tag{15}$$

$$\left[\frac{\partial X_5}{\partial t}\right]_{decay} = -\nu_{X_5 dec} \cdot X_5 \qquad (16)$$

The values of the stoichiometric, kinetic, switching function and denitrification parameters are listed in Table 3. Most of these parameters were taken from previous studies (Schäfer et al., 1998; Eljamal et al., 2007).

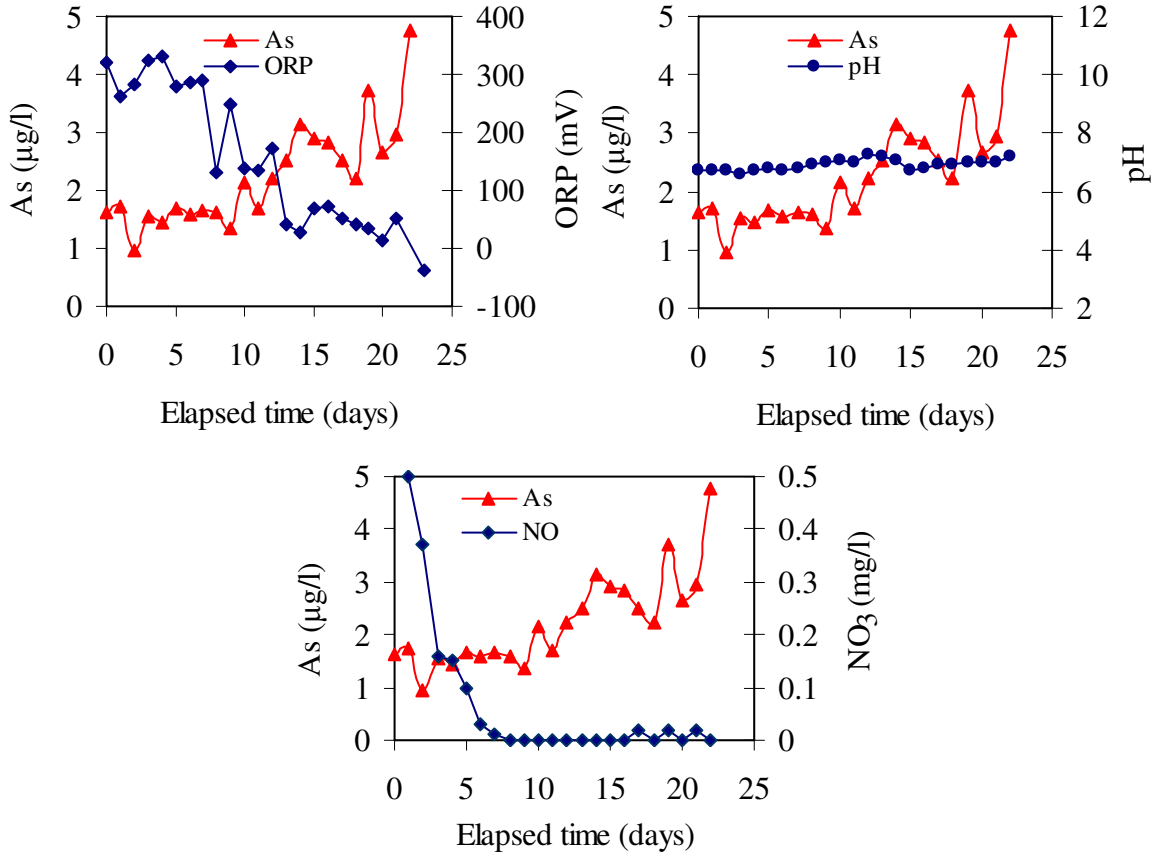

Figure 3. Relationships of As with **a** ORP, **b** pH and **c** NO_3^- in the effluent.

4. RESULTS AND DISCUSSION

4.1 Relationship of As with ORP, pH and NO_3^-

Geochemical factors are exerts an important role in the release of arsenic in the soil. The redox conditions observed in the present study can be classified (1) highly aerobic conditions (>250 mV), (2) moderately aerobic (100 to 250 mV) and moderately anaerobic (-100 to +100 mV). In the system, water flow was continuous from feeding tank to overflow tank for creating the anaerobic condition in the soil column. The leaching profile of arsenic as a function of oxidation reduction potential (ORP) is presented in Fig. 3a. Leaching of As in aerobic conditions is insignificant and coprecipitation or sorption of As on to Fe precipitates can limit arsenic

solubility (Nikolaidis et al. 2004). Dissolved As concentration increased gradually from 2.84 to 4.76 µg/l over range of ORP (73 to -37 mV). The influence of redox on As solubility in soils was found (Masscheleyn et al. 1991) to be governed by (i) reduction of arsenate to arsenite followed by desorption and (ii) the dissolution of Fe-oxyhydroxides and concurrent release of coprecipitated arsenate. The increase of As solubility in moderately reducing condition was probably linked to the reductive dissolution of hydrated iron oxides. However, unfortunately, the speciation of As could not perform due to the low concentration.

The effluent of soil column pH is circum-neutral and range between 6.6 and 7.3 (Fig. 3b). The influence of pH on As release in soil is discussed later in this section. The concentration of NO_3^- decreased from 14.91 mg/l to 0.01 mg/l with elapsed time and demonstrated negative correlation with As (Fig. 3c). The concentration of NO_3^- decreased with time in the effluent may be due to process resulting from microbially mediated reduction in presence of organic matter in the soil (Komor and Anderson 1993). Bhattacharya et al. (2002) suggests that the organic matter rich sediments mostly reducing in nature can create favorable conditions for forming reducing bacteria, thereby decreasing the concentrations of NO_3^- in water (Akai et al. 2004).

Batch experiments were carried out at pH of 1-13 with a liquid:solid ratio of 60:1 to observe the influence of pH on the solubility of As in the soil. Though the solution concentration, reaction time and soil-to-liquid ration can strongly influence As extraction patterns (Chappell et al. 1995), the different reaction conditions have also been observed in the previous studies (Carbonell-Barrachina et al., 1999; Cai et al., 2002; Ruiz-Chancho et al., 2005; Alam and Tokunaga, 2007). Results from present experiments for arsenic and iron are shown in Fig. 4. The extracted contents of As and Fe are generally much lower than the total metal concentration and exhibited a strong pH dependence. With an increase in pH from 1 to 7, As and Fe concentrations drops an order in magnitude with the total dissolved As and Fe concentrations decreasing from 271.3 µg/l and 750.7 mg/l to 18.73 µg/l and 92.6 mg/l, respectively. Further increase in pH to 13 of the suspension increased the dissolved metal concentration by two orders of magnitude. Maximum As and Fe leaching was observed at highly alkaline conditions (pH 13), with dissolved concentrations as high as 2651.03 µg/l and 1003.2 mg/l, respectively.

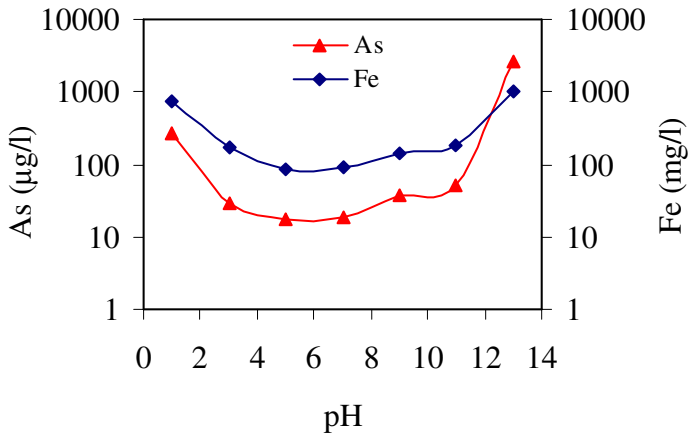

Figure 4. Influence of pH on the release of arsenic and iron in the soil.

The content of As and Fe extracted from soil can be attributed to either dissolution of less resistant minerals or sorption/desorption mechanisms which are influenced by the pH. The dissolved As concentration at very low pH indicating either release of weakly sorbed As on Fe

oxides or dissolution of carbonates driven by cation exchange (Pierce and Moore 1982; Masscheleyn et al. 1991; Bayard et al. 2006) The similarities in the leaching profiles of As and Fe due to its release from their acid extractable phases suggested a strong association between them. With an increase in pH to neutral pH, precipitation of Fe as hydroxides can result in coprecipitation of arsenic on to the solid matrix, resulting in lower concentrations of dissolved arsenic.

With an increase in pH beyond neutral pH, almost 0.55% of the total As was released at pH 11, while 28.2% of total As was released at pH 13. In contrast, less than 2.6% of total Fe was released under alkaline conditions. As the suspension pH increases, hydroxyl ions replace As on the iron oxide sorption sites, facilitating the desorption of As oxyanions (Pierce and Moore 1982; Masscheleyn et al. 1991; Yang et al. 2002). The relatively small amount of Fe released is due to the reductive dissolution of iron oxides, which may contribute to As solubilization (Stumm and Morgan 1996; Carbonell-Barrachina et al. 2004). While, McArther et al. (2004) found that pH dependent desorption of As is likely to be insignificant in groundwaters for which pH is greater than 8.5, and only occur via contact of high pH (10) landfill leachates with aquifer substrate.

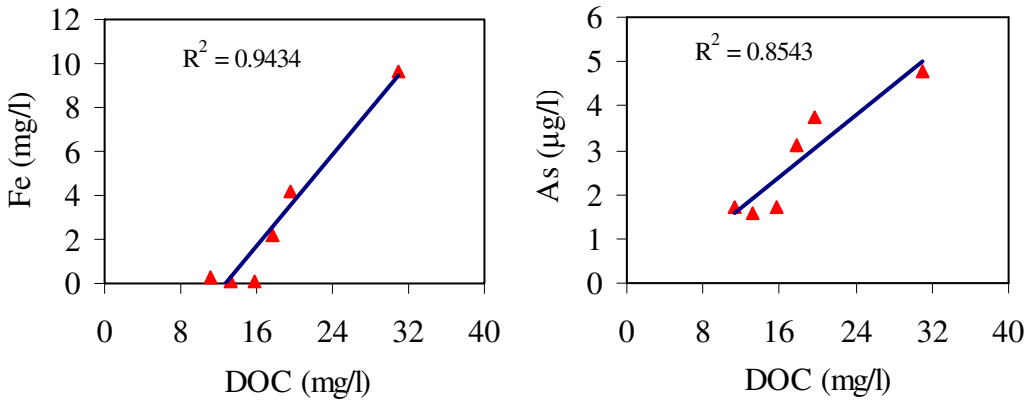

Figure 5 Relationship between the concentrations of DOC with (**a**) Fe and (**b**) As in the effluent.

4.2 Correlation of As with other parameters

Degradation of organic matter could drive the sequence of redox reactions in the aquifer and may, thereby enhance As mobilization (Ravenscroft et al. 2001; Anawar et al. 2003; McArthur et al. 2004). Elevated level of Fe due to biodegradation of organic matter (Harvey et al. 2002, Bhattacharya et al. 2006) are also indicated by strong correlation (R^2 = 0.9434) of DOC with Fe (Fig. 5a). Strong correlation (R^2 = 0.8543) between DOC and As (Fig. 5b) in effluent of soil column suggests that the microbial degradation of organic matter in the soil results in an moderately reducing environment and facilitates the release of As in the water (McArthur et al. 2001). Aiken (2002) pointed out that the DOC produce through the biodegradation of organic matter in the aquifer. A significant portion of the refractory DOC remains for a longer time in the liquid phase. Enhanced microbial activity accelerates the diagenetic process, involving mobilization of As from soils and sediments with high organic matter (Akai et al. 2004; Bhattacharya et al. 2006).

Biodegradation of organic matter drives extreme degrees of reduction of Fe-oxyhydroxide and supplies high concentrations of As to groundwater (Ravenscroft el al. 2001). The correlation

of As with Fe (R^2 = 0.7932) is stronger than that of the correlation between As and Mn (R^2 = 0.4612) again suggests that As is released in effluent due to reductive dissolution of Fe-oxyhydroxide and this reduction is coupled to the microbial degradation of organic matter in the soils (Fig. 6a, b).

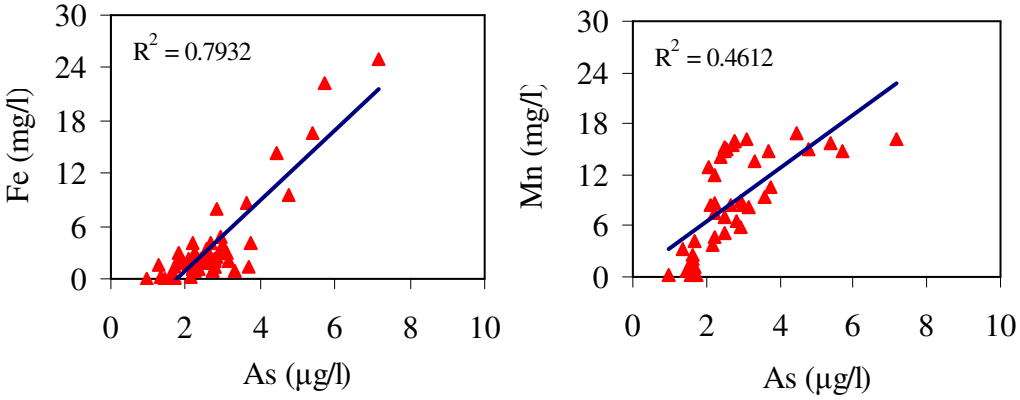

Figure 6. Relationship between the concentrations of As with **a** Fe and **b** Mn in the effluent.

4.3 Comparison between measured and simulated concentrations

The measured concentrations of Mn, Fe and As in the effluent of soil column compared with the output of microbially-mediated biogeochemical arsenic transport model, which shown in Fig. 5. The measured and simulated concentrations of Mn, Fe and As increased with elapsed time and fairly agreements with each other (Fig. 7a, b and c, respectively). However, some discrepancies exist between measured and simulated concentrations of them. A possible explanation for these discrepancies is that the aerobic and denitrifying bacteria *X1* (Table 2) completely reduced oxygen and nitrate in the model, however, the observed oxidation-reduction potential values (Fig. 3a) indicated that the moderated reducing conditions present in the experimental soil column. Moreover, the reduction of As(V) is generally inhibited in presence of oxygen, nitrate, Mn(IV) or Fe(III), because oxygen, nitrate, Mn(IV) and Fe(III) reducers derive more energy from the organic matter than the As(V) reducers. The oxidation of degradable organic carbon with solid Mn(IV) as electron accepter is catalyzed, e.g., by the anaerobic bacterial GS-15 or by *Alteromonas Putrefaciens* (Lovely and Phillips, 1988). These microorganisms are also able to reduce solid Fe(III) (Schäfer et al. 1998). In the model, manganese and iron reducers are two different bacterial groups. Manganese reducer in the model oxidizes CH_2O to carbon dioxide and reduces Mn(IV) from MnO_2 to Mn(II) ions. The bacteria growth rate and exchange coefficient were tuned until the simulated manganese reduction resulted in the observed dissolved Mn(II) concentration became close.

The microbial Fe(III) reduction rate cannot directly be determined from observed dissolved Fe(II) concentration. von Gunten and Zobrist, (1993) determined a microbial Fe(III) reduction rate in an additional column experiment, where no Fe-As compound was present. The most important model parameter was the exchange coefficient between solid Fe-As and microbially available Fe-As in the biophase (Fig. 2). Again the bacteria growth rate was tuned until the simulated arsenic concentration became close to the observed dissolved arsenic concentration (Fig. 7c). Several controlled laboratory studies have been performed to understand the release

mechanism of arsenic species in groundwater from various types of soil mineral and sediment. Islam et al. (2004) suggested that arsenic adsorbed onto sediment surfaces could be mobilized into groundwater by anaerobic respiration of Fe(III) reducing bacteria. In other study, Newman et al. (1998) found that the As(V) reducing bacterium, *D. auripigmentum* could reduce As(V) to As(III).

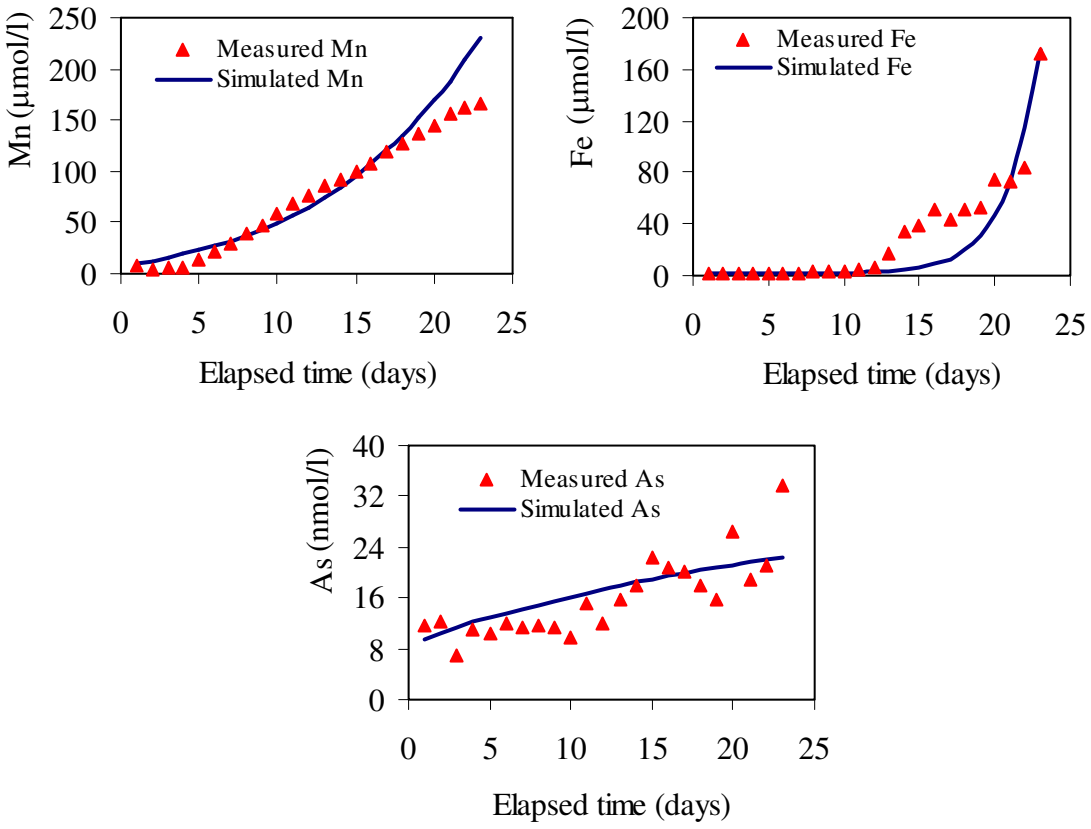

Figure 7. Comparison of the measured concentrations of Mn, Fe and As with those obtained from the microbially-mediated biogeochemical model in **a**, **b** and **c**, respectively.

5. CONCLUSION

Experiments were carried out to observe the influence of geochemical factors on As mobilization from soil into water. The concentration of total As and As(V) measured in study soil was same that indicated As remained primarily as As(V) in soil. The results of this study demonstrate that the moderately reducing condition of soil column and strong correlation of As with DOC and Fe suggests that the microbially mediated degradation of organic matter and reductive dissolution of Fe-oxyhydroxide is considered to be the dominant processes to release As in aquifers.

Batch pH leaching studies showed a strong dependence of pH on both As and Fe leaching. Arsenic mobilization was high under highly acidic conditions and maximum in the alkaline pH region. Its mobilization was strongly correlated with that of iron, indicating that As release occurred either via (i) dissolution of the Fe-oxyhyroxide bearing phase in the acidic region or;

(ii) desorption or reductive dissolution of Fe oxide in the alkaline region. Near the neutral pH region, significantly low As and Fe release was observed, due to As re-precipitation on Fe.

A reactive transport model for describing the microbially mediated transformation of arsenic species and their subsequent transport was developed. Simulation results of this model well matched those found experimentally. The developed model can serve as a useful tool for predicting the fate and transport of arsenic species in groundwater systems considering bacteria mediated oxidation and reduction bio-chemical processes.

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